STRUCTURAL INFORMATION INFERENCE FROM LANTHANOID COMPLEXING SYSTEMS: PHOTOLUMINESCENCE STUDIES ON ISOLATED IONS

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The application of lanthanoid complexes ranges from photovoltaics and light-emitting diodes to quantum memories and biological assays. Rationalization of their design requires a thorough understanding of intramolecular processes such as energy transfer, charge transfer, and non-radiative decay involving their subunits. Characterization of the excited states of such complexes considerably benefits from mass spectrometric methods since the associated optical transitions and processes are strongly affected by stoichiometry, symmetry, and overall charge state. We report herein spectroscopic measurements on ensembles of ions trapped in the gas phase and soft-landed in neon matrices. Their interpretation is considerably facilitated by direct comparison with computations.

The combination of energy- and time-resolved measurements on isolated species with density functional as well as ligand-field and Franck-Condon computations enables us to infer structural as well as dynamical information about the species studied. The approach is first illustrated for sets of model lanthanoid complexes whose structure and electronic properties are systematically varied via the substitution of one component (lanthanoid or alkali,alkali-earth ion): (i) systematic dependence of ligand-centered phosphorescence on the lanthanoid(III) promotion energy and its impact on sensitization, and (ii) structural changes induced by the substitution of alkali or alkali-earth ions in relation with structures inferred using ion mobility spectroscopy. The temperature dependence of sensitization is briefly discussed. The focus is then shifted to measurements involving europium complexes with doxycycline an antibiotic of the tetracycline family. Besides discussing the complexes' structural and electronic features, we report on their use to monitor enzymatic processes involving hydrogen peroxide or biologically relevant molecules such as adenosine triphosphate (ATP).